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# ASIAN DEVELOPMENT BANK

## ENERGY EFFICIENCY SUPPORT PROJECT

SECTOR ANALYSIS
CHLOR-ALKALI INDUSTRY

SUPPORTED BY
GOVERNMENTS OF THE NETHERLANDS AND INDIA

EXECUTING AGENCY
THE INDUSTRIAL CREDIT AND INVESTMENT CORPORATION OF INDIA LIMITED

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# Contents

# Contents

# Executive Summary

The Government of Netherlands (through the Asian Development Bank) and the Government of India has jointly launched a project entitled ' Energy Efficiency Support Project (ESP)' to look into the various aspects of energy and environmental issues pertaining to the Indian Industry. The project comprises of two distinct phases. Phase-I of the project deals with identification of industry sectors where there is a substantial scope for energy saving and pollution reduction through energy efficiency investments. Phase-II of the project primarily covers various initiatives like undertaking energy and environmental audits, feasibility studies, training programmes and promotional campaigns for industry sectors identified under the phase-I of the study. One of the sectors covered for detailed analysis by TERI under phase-I of this project is the chlor-alkali sector.

The Indian chlor-alkali industry represents about 2.5% of the total world production at present and produce three major inorganic chemicals, namely caustic soda, chlorine, and soda ash. These chemicals has widespread use in industries like soaps and detergents, fibres and plastics, glass, petrochemicals, pulp and paper, fertilizers, explosives, solvents, textiles and other chemicals. The alignment of the Indian chlor-alkali industry with its international counterpart is expected to elevate chlorine to a mainstream product and render caustic soda as a useful byproduct. The use of most chlorosolvents can be expected to decline due to public health concerns. The energy costs per tonne of caustic soda and soda ash manufacture has risen considerably over the years and are being covered under the present assessment.

## Caustic soda

There are 27 major caustic soda plants in the country with a total installed capacity of 1.37 million tonnes. Out of the 27 plants, two plants are government owned and two are in joint sector. The remaining 23 plants are in the private sector. In India, four different processes viz. mercury cell, membrane cell, diaphragm cell and chemical process are used for the production of caustic soda. As per the estimates carried out in 1992-93, the mercury cell accounts for 77% of total caustic soda production followed by membrane cell, whose share is 12%.· Caustic soda manufactured by the diaphragm cell process represents only 8% of the total production. The chemical process accounts for the remaining 3% production. The most energy efficient and environmentally friendly caustic soda manufacturing process is through the membrane cell route. It produces caustic lye of 30% concentration with a specific energy consumption of 3235 kWh/t. The most polluting

caustic soda (50% concentrated lye) production process is mercury cell with a specific energy consumption of 3420 kWh/t. The specific energy consumption in the diaphragm process is 3900 kWh/t. The absolute consumption of electrical energy and thermal energy in the sub-sector in 1990-91 were 3015 mil.kWh and 406300 mil. kcal respectively.

Overall energy saving potential in this sub-sector is estimated at 15%. The major energy conservation measure that can be adopted by the sub-sector is to convert mercury/diaphragm cell process to membrane cell. Converting a typical 100 tpd plant based on mercury cell technology to membrane technology, would entail an investment of about Rs 25 crores. The estimate is based on a case study prepared in 1989-90.
The major pollutants emitted from diaphragm and mercury cell-chlorine plants include chlorine, mercury vapours and carbon monoxide. Of this, mercury emission both in gaseous form and alongwith liquid effluent is a source of major concern. The average mercury discharge alongwith liquid effluent in the Indian chlor-caustic units have been observed to be more than 100 gm/t as compared to 20 gm/t in advanced countries. Mercury vapour is emitted with the gaseous streams also. The specific solid pollutants generated in the diaphragm process is minor in quantity which could be controlled with bag filters.

Government of India has reduced the custom duty from 35% to 25% for membrane cell technology and 20% reduction in the custom duty for the import of membrane. Therefore, the caustic soda sub-sector of the industry is addressing to the long overdue task of upgradation of technology by conversion to energy and non-polluting membrane cell technology and change in product mix in line with the international standards.

## Soda ash

The commercial production of soda ash in India started in early thirties. The Indian soda ash industry have developed to such an extent that the country is not only self-sufficient but has surplus capacity. The industry has entered into the export market since 1991-92. Out of the six soda ash manufacturing units in India, three units are based on solvay process, two units follow modified solvay process (dual process) and the sixth one uses AKZO drylime process. The total installed capacity of the sub-sector is 1.39 million tonnes as of March 1995 which includes installed capacity of the recently installed seventh plant, VXL India Ltd., Porbandar, Gujarat. The capacity utilisation of this sub-sector remained high at 110.8% between April 1994 to February 1995.

The two major energy consuming areas in the solvay process are (i) calcination section for the conversion of bicarbonate to soda ash and (ii) ammonia distillation section for the recovery of ammonia from ammonium chloride. These two areas together consume nearly 70% of the total energy required in the process. Calcination of limestone

is not required in dual process. The specific steam in Solvay process, AKZO dry lime process and the dual process are 3.5, 2.12, 2.2 tonnes/tonne of caustic soda respectively. The corresponding electricity consumption being 150, 180-200 and 400 kWh/tonne of caustic soda production. The total energy consumption in the sector during April 1994 - February 1995 was 476643 Gcal.

Overall energy saving potential in this sub-sector is estimated at 15%. The major energy conservation schemes applicable for this sector are; (i) Use of improved heat exchangers for ammonia recovery system for soda ash production; (ii) Use of dry lime in ammonia still for heat recovery in soda ash production.

Based on an assessment of the sector and its comparative evaluation with the other sectors studied under the phase-I study, chlor-alkali sector is not considered to be an ideal candidate for phase-II of the project.

CHAPTER 1

# Introduction

Indian chlor-alkali industry witnessed a significant growth, since its inception. Average growth rates had been as follows:

- 12.8% during sixties;
- 7.5% during seventies;
- 5.7% during early eighties.

The end use industries consuming alkali products as inputs have grown at a fast rate during the post-independence period. Among others they include rayon, viscose fibre, paper and pulp, and aluminium. Historically, the pattern of chlor-alkali demand-supply cycles has differed during periods of strong and weak economic growth. This cyclic pattern would be more predominantly favouring chlorine in the years to come due to the current government policies of globalisation. However, rising chlorine production and increasing chlorine prices impact directly on the caustic soda market where supply lengthens, inventories grow and prices fall. Caustic soda demand eventually catches up but, by then, economic growth has slowed and recession has set in.

This industry represents about 2.5% the total world production at present and produce three major inorganic chemicals, namely

- Caustic soda (sodium hydroxide - $NaOH$)
- Chlorine ($Cl_2$)
- Soda ash (sodium carbonate - $Na_2CO_3$)

There are as many as 19 such products. The raw materials requirement and the end users of chlor-alkali industry products are given in **figure 1.1**.

The cost of energy per tonne of caustic soda and soda ash (based on the solvay process) has risen considerably since 1973. The trend in energy prices ( Cost of energy per tonne of output as percentage of per tonne realisation) in the sub-sectors is significant.

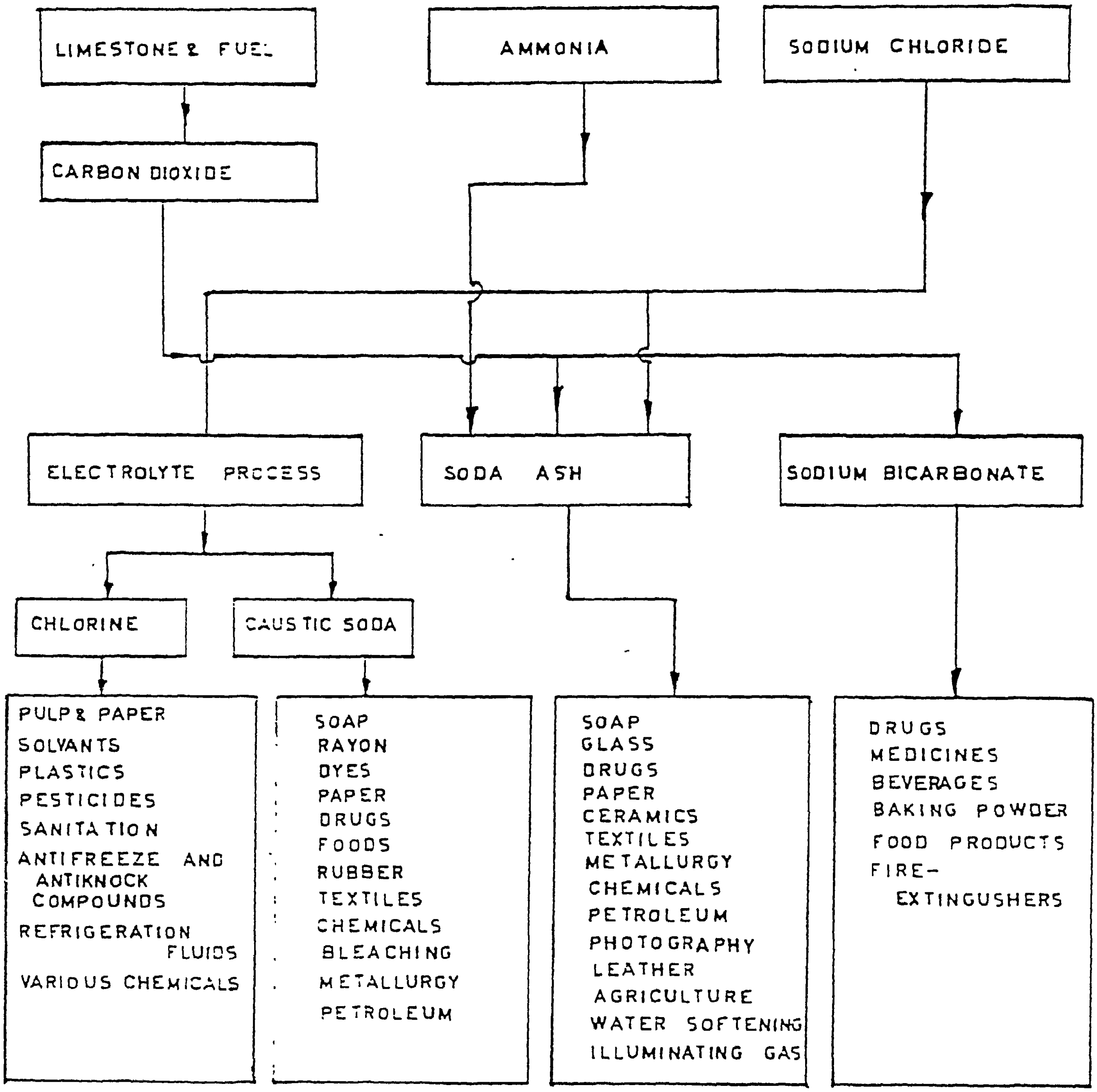



**FIG 1.1: RAW MATERIALS & END USERS OF CHLOR ALKALI INDUSTRY PRODUCTS**

CHAPTER 2

# Sector profile

## 2.1 Overview of chlor-alkali industry

Chlorine is obtained as a by-product in the caustic soda manufacturing. Three chemicals caustic soda, chlorine and soda ash have widespread use in industries for the production of soaps & detergents, fibres & plastics, glass, petrochemicals, pulp & paper, fertilisers, explosives, solvents, textiles and other chemicals. Their utilization for various high value added chemicals has recently been started in the Indian chemical industry.

The importance of chlorine for the chemical industry stems from the fact that it is highly reactive element and reacts easily with the slow reacting petrochemicals. Chlorinated solvents or chlorine based solvents are either proven or suspected carcinogens. The use of most chlorosolvents can be expected to decline due to public health concerns. The only significant strength for chlorine demand appears to be in the resurgence of the PVC (polyvinyl chloride) industry. Worldwide, it is true that major chlorine consuming industry is PVC (except Canada and some other small countries).

## 2.2 Caustic soda industry sub-sector

The commercial production of caustic soda with electrolysis process in India dates back to 1941. However, this sub-sector witnessed a rapid growth only from 1955. There are 27 major caustic soda plants in the country with a total installed capacity of 1,378,950 tonnes. Out of the 27 plants, two plants are government owned and two are in joint sector. The remaining 23 plants are in the private sector.

Theoretically chlorine production is 900 kg. per tonne of caustic soda or 1.13 tonne of caustic soda produced for every tonne of chlorine produced during the electrolysis of brine. In practice about 875 kg of chlorine is produced per tonne of caustic soda production. The product with the diaphragm process is contaminated with salt to the extent of about 1% and hence makes it unsuitable for use in the single largest consumer of caustic soda in rayon industry.

### *2.2.1 Production details*

In India, four different processes viz. mercury cell, membrane cell, diaphragm cell and chemical processes are used for the production of caustic soda. As per the estimate carried out in 90/91, the mercury cell accounts for 82% of total production followed by membrane cell, whose share is 11.4%. Caustic soda manufactured by the Diaphragm cell process represents only 6.5% of the total production. The chemical process accounts for only

0.1%. Similar estimates in 1992-93 revealed the production of caustic soda at a rate of 77%, 12%, 8% from mercury, membrane, diaphragm cell processes. Rest is from chemical process. The time series performance and the capacity utilisation of the caustic soda units is shown in **table 2.1.** As can be seen from table 2.1, the capacity utilisation has always been more than 64% and achieved a maximum of 96.9% during 1970. The decline in capacity utilisation of caustic soda industry during 1975-1990 can be attributed to problem of chlorine utilisation and shortage of graphite anodes. However, the corresponding figure till February 1995 is 90.3%.

**Table 2.1.** Capacity utilisation of caustic soda plants

| Year | Installed capacity ('000 tpa) | Production ('000 tpa) | Capacity utilisation (%) |
|---|---|---|---|
| 1955 | 45.0 | 34.8 | 77.3 |
| 1960 | 121.1 | 98.3 | 81.2 |
| 1965 | 268.6 | 214.9 | 80.0 |
| 1970 | 368.9 | 357.4 | 96.9 |
| 1975 | 617.0 | 458.0 | 74.2 |
| 1980 | 826.5 | 553.0 | 66.9 |
| 1985 | 1091.6 | 709.4 | 64.9 |
| 1990 | 1258.3 | 970.6 | 77.2 |
| 1995* | 1378.9 | 1245.0 | 90.3 |

*Source:* Technology evaluation in caustic soda industry, DSIR, 1992

The time series data with respect to total production of caustic soda starting from the year 1987-88 is given in **table 2.2** alongwith the total production figure, the share of production through different processes/units also presented to give an idea of the relative importance of each production. The noteworthy observation in table 2.2 is the fact that the share of membrane process, which is an energy efficient and environmentally friendly process compared to the conventional mercury process has grown by, 86.23% over the 5 year period from 1987/88 - 1991/92.

*upto February 1995 from Market and Market Shares, CMIE*

**Table 2.2.** Process-wise caustic soda production data (in tonnes)

| Year | Membrane process | Mercury process | Diaphragm process | Total |
|---|---|---|---|---|
| 1987-88 | 12918 (1.66) | 708040(91.01) | 56976(7.33) | 777934 |
| 1988-89 | 31210 (3.55) | 782200(89.25) | 63000(7.2) | 876410 |
| 1989-90 | 103973 (10.93) | 778559(81.7) | 70279(7.37) | 952811 |
| 1990-91 | 115774 (11.4) | 834990(82.1) | 66184(6.5) | 1016948 |
| 1991-92 | 155406 (14.75) | 845939(80.3) | 52127(4.95) | 1053472 |

Source: Technology evaluation in caustic soda industry, DSIR, 1992

Note: Figures in brackets indicate the share of total production. Yearly production of caustic soda using chemical process is not available.

The total production of caustic soda is 1101800 MT and 1115300 MT in the year 1992-93 and 1993-94 respectively.

## *2.2.2 Export details*

Caustic soda is exported as flakes to the neighbouring South Asian countries and the Gulf countries. The time series data on export is given in **table 2.3.**

**Table 2.3.** Export details of caustic soda (in tonne)

| Year | 1987-88 | 1988-89 | 1989-90 | 1990-91 | 1991-92 | 1992-93 | 1993-94 |
|---|---|---|---|---|---|---|---|
| Exported quantity | 9,940 | 15,700 | 10,000 | 12,000 | 22,000 | 25,000 | 22,000 |

Source: Annual report (1993-94) of Alkali Manufacturers' Association

The export of higher quantity was not possible due to sudden drop in international prices of caustic soda.

## *2.2.3 Demand projections*

During 9th Five Year Plan period, the demand for caustic soda is expected to grow at a rate proportional to the growth rate of the principal end use industries such as paper & paper board, aluminium, soaps, cotton textiles and viscose staple fibres. The estimated demand projections for caustic soda during 2000 A.D. is given in **table 2.4.**

**Table 2.4.** Estimated demands of caustic soda for 2000 A.D.

| S. No | Source | Projected demand (mil. tonnes) |
|---|---|---|
| 1 | DSIR report | 1.365 |
| 2 | Perspective Plan for chemical industry | 1.400 |

*Source: Technology evaluation in caustic soda industry, DSIR, 1992*

Projections in the Hindu Survey of Indian industry report in 1994 and 1995 are as follows:

The total liquid chlorine consumption is expected to increase from 506000 Mt in 1988 to 653000 Mt in 1995, 812000 Mt by 2000 A.D. and to about 19 lakh tonnes by 2002-03.

## 2.2.4 Process description

Chlorine and caustic soda are produced concurrently by the electrolysis of the brine in either the diaphragm/mercury/membrane cell. These are electrolytic processes. Lye of caustic soda is produced at the concentration of 30% from the membrane cell, 50% from the mercury cell and 11% from the diaphragm cell.

The latest development in the electrolysis process is the membrane cell technology. The demand levels for both caustic soda and chlorine have been linked to the levels of activity in the consuming sectors, and has shown increasing over the years.

### *2.2.4(i) Diaphragm cell process*

In Diaphragm cell, an asbestos diaphragm is employed on the outside of the cathode of the cathode screen, which separates the cell into two compartments, one containing the anode and the other the cathode. The sodium chloride solution (brine) enters the anode compartment and completely covers the anodes and cathode tubes. The chlorine leaves the cell through an outlet in the cell head. The anolyte flows through the diaphragm into the cathode compartments because of the difference in liquid level between the two compartments. The catholyte is a solution of sodium chloride and sodium hydroxide. The hydrogen produced in the same time leaves the cell through an outlet in the cathode. The cell liquor (i.e. mixture of sodium chloride and sodium hydroxide) overflows the cell through a level control pipe on the cathode. A schematic diagram of the diaphragm cell process for the production of caustic soda is shown **figure 2.1.**

### *2.2.4(ii) Mercury amalgamation process*

In mercury cell, moving mercury acts as cathode. On top of the mercury is flowing concentrated brine with a sodium chloride capacity of 310 gpl. Anodes are placed in the brine so that there is a small gap between the anode and the mercury cathode. Sodium ions get deposited and form sodium-mercury amalgam. The concentration of amalgam is maintained at 0.2-0.4% sodium, so that the amalgam flows easily. The chlorine gas and the depleted brine (270 gpl) flow out of the cell. The amalgam flows out of the cell through a weir and into the decomposer. The amalgam may be passed through a water wash between the cell and the decomposer to remove traces of sodium chloride. The amalgam flows through the decomposer counter-current to the flow of demineralised water

in the presence of a catalyst to produce sodium hydroxide and hydrogen. Stripped of its sodium, the mercury flows out of the lower end of the decomposer and is recirculated through pump back into the cell. A block diagram of the mercury cell process for the production of caustic soda is given **figure 2.2.**

*2.2.4(iii) Membrane cell process*

In the membrane process, the anolyte and the catholyte are separated by a cation exchange membranae that selectively transmits sodium ion but suppresses the migration of hydroxyl ion from the cathode into the anolyte. $H^+$ and $OH^-$ ions are also transmitted. Saturated brine is fed into the anode compartment where chlorine gas is evolved at the anode and sodium ions migrate into the catholyte through the membrane. Depleted brine is discharged from the anolyte chamber of the cell. In the cathode compartment, hydrogen is evolved at the cathode, leaving hydroxyl ions, together with the permeating sodium ions, constitute the caustic soda. Pure water is added to the catholyte the concentration of caustic soda. Chlorine ions in the anolyte are exclude by the cation exchange membrane so that the rate of diffusion of chloride from the anolyte to the catholyte is extremely low. As a result, a strong caustic (32-35% wt/wt) with low salt content, less than 100 ppm is obtained as the catholyte effluent. Since the catholyte is a strong caustic, there is some back migration of hydroxyl ions from the catholyte into the anolyte, even with the use of a high performance cation exchange membranae. This causes a loss of current efficiency 3.5% in caustic production. A block diagram of the membrane cell process for the production of caustic soda is given **figure 2.3**.

## 2.3 Soda ash industry sub-sector

Soda ash (sodium carbonate) is the most widely used chemical in industries such as soaps, detergents and glass. It is also finds application in industries such as sheets/hollow-wares/sleeves/tubes, paper, textile, dyes & dyestuffs, sodium silicate, sodium bicarbonate and sodium dichromate. It is also used in laundries for purification of water and an auxiliary chemical in industries like resins, vanaspati, and petroleum. The various grades of soda ash along with their respective application areas are listed in **Table 2.5**.

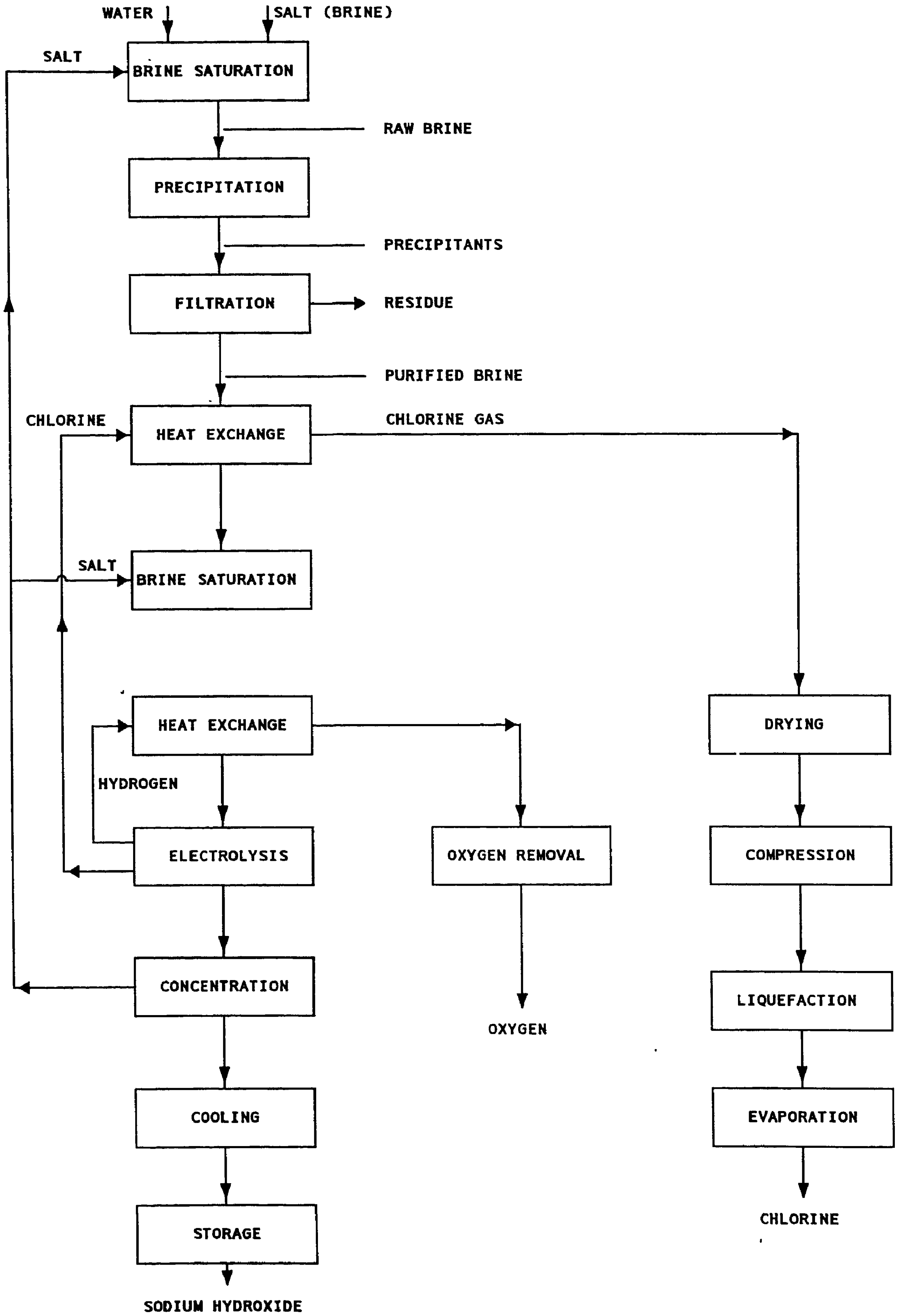



FIG 2.1 DIAPHRAGM PROCESS

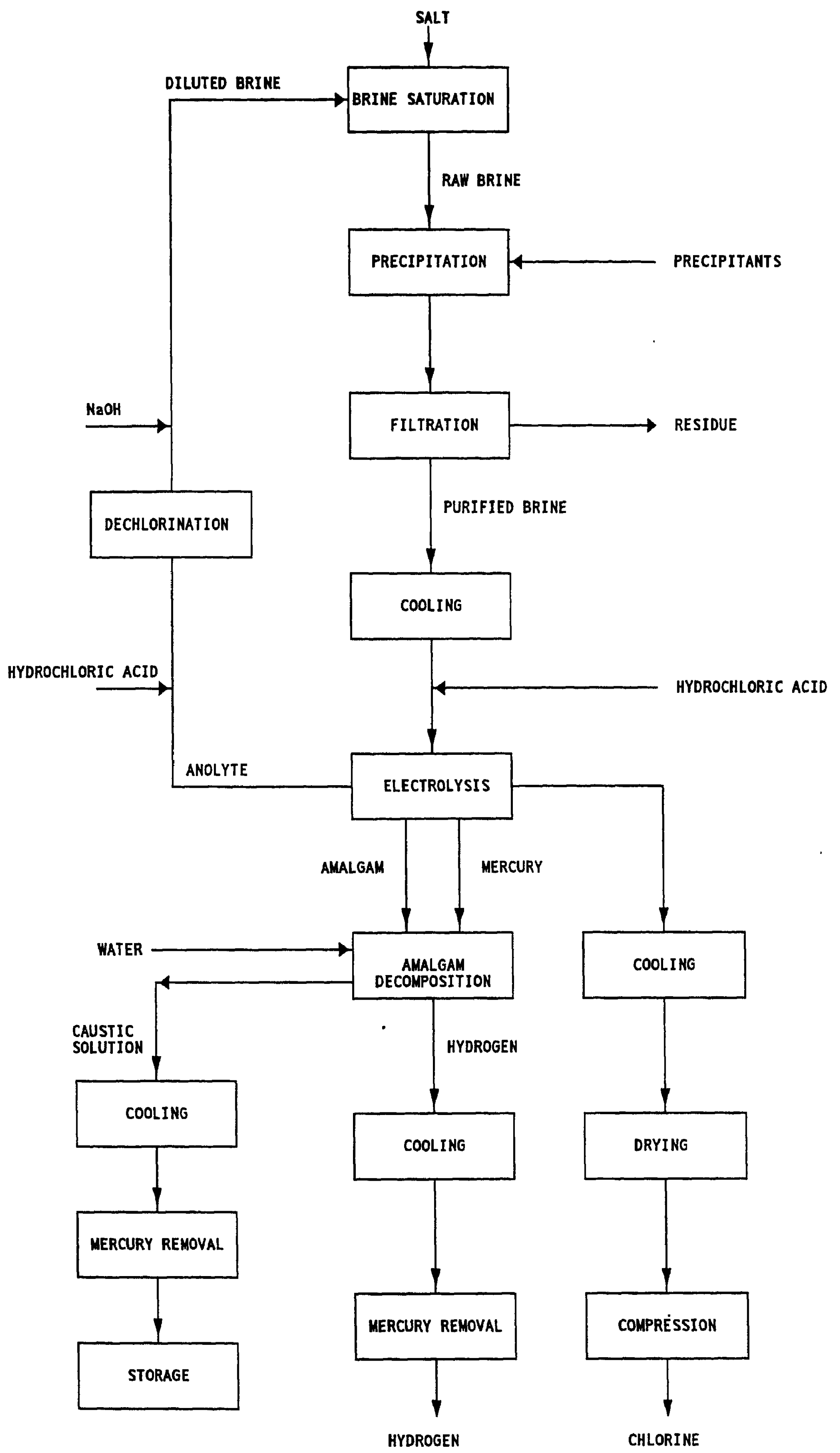



FIG 2.2 MERCURY CELL PROCESS

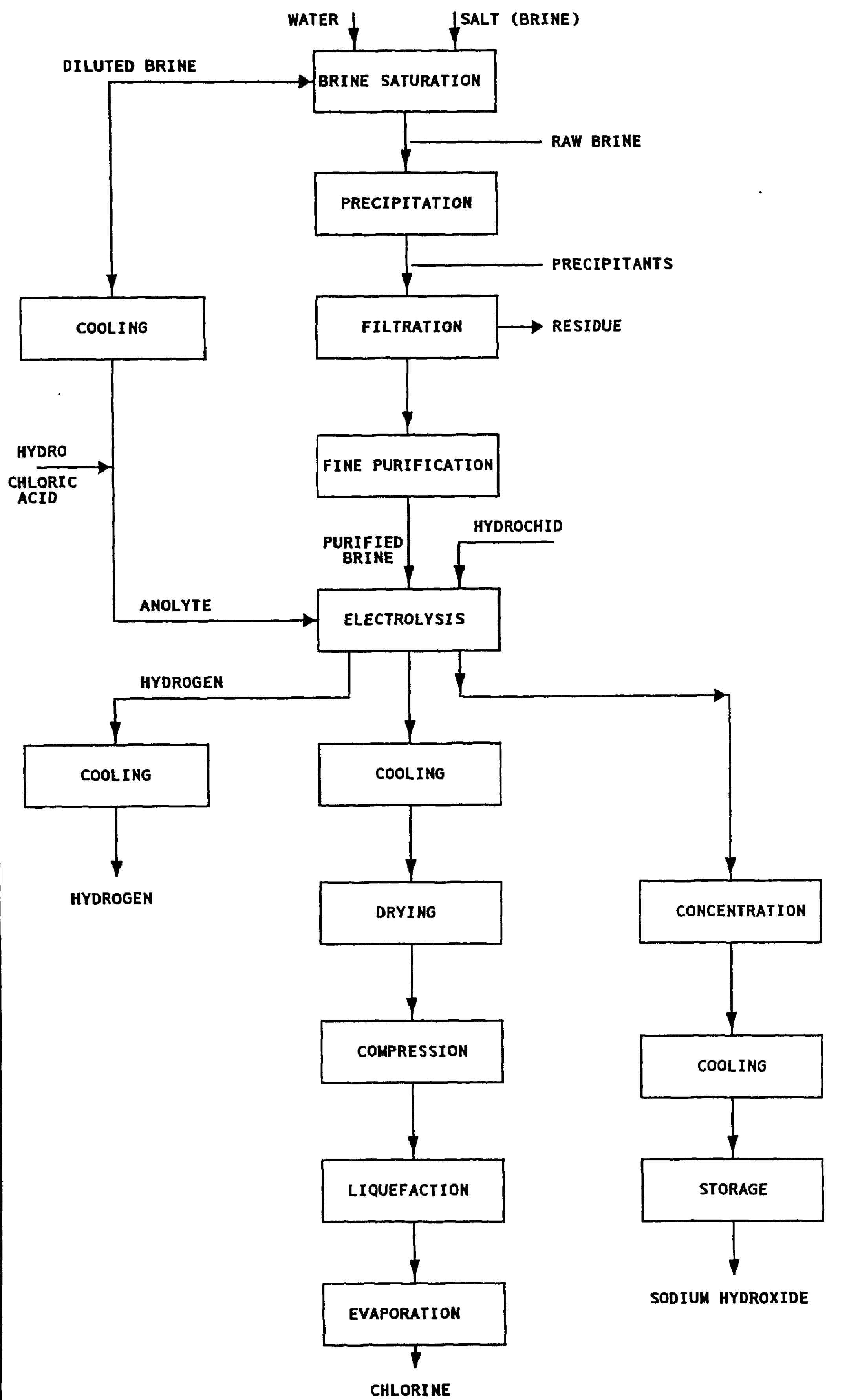



FIG 2.3 MEMBRANE CELL PROCESS

**Table 2.5.** Commercial types of soda ash

| S. No | Type | Bulk density (gm/lit) | Application areas |
|---|---|---|---|
| 1 | Light | 500-750 | Household, soaps, detergent |
| 2 | Medium | 751-950 | Glass, silicate, bichromate |
| 3 | Dense | 951-1250 | Glass, silicate, bichromate |
| 4 | Granular | 1050-1100 | Steel, metal refining, jaggery |

Source: Technology evaluation & norms study in soda ash industry, DSIR (1993)

### *2.3.1 Production details*

The commercial production of soda ash in India started in early thirties. However, the real growth in the sector happened only after sixties. At the end of first Five Year Plan (1955-56), the installed capacity of soda ash was only 90,000 tonnes which increased in subsequent plans and reached a figure of 1.51 million tonnes at the end of seventh Five Year Plan (1989-90). The growth rate in soda ash production can be seen from table 2.6 which gives a time series data since 1980-81. Along with the installed capacity, the actual production and the capacity utilisation figures are also provided in the same table. As can be seen, the capacity utilisation was quite high, averaging at 87.7% for the 15 years.

**Table 2.6.** Growth in installed capacity and production

| Year | Installed capacity ('000 t) | Production ('000 t) | Capacity utilisation (%) |
|---|---|---|---|
| 1980-81 | 633 | 570 | 90.0 |
| 1981-82 | 665 | 632 | 95.1 |
| 1982-83 | 746 | 635 | 85.1 |
| 1983-84 | 886 | 778 | 87.8 |
| 1984-85 | 1004 | 820 | 81.7 |
| 1985-86 | 1004 | 926 | 94.6 |
| 1986-87 | 1004 | 976 | 97.2 |
| 1987-88 | 1549 | 1016 | 65.5 |
| 1988-89 | 1549 | 1227 | 79.2 |
| 1989-90 | 1549 | 1402 | 70.5 |
| 1990-91 | 1549 | 1416 | 91.4 |
| 1991-92 | N.A. | 1190 | N.A. |
| 1992-93 | 1554 | N.A. | N.A. |
| 1993-94* | 1492 | 1365 | 91.5 |
| 1994-95** | 1393 | 1544 | 110.8 |

Source:

1. Annual reports of Chemical Weekly
2. Market & Market Shares, CMIE

* *upto February 1994*
** *upto February 1995*

At present, there are seven soda ash manufacturing industries in India with a total installed capacity of 13,93,250 tonnes. A list of soda ash manufacturing units with their installed capacities are given in **table 2.7.**

As can be seen from table 2.7, the latest plant was set up in 1988 and the oldest being commissioned in 1932.

## 2.3.2 *Import/export details*

The Indian soda ash industry have developed to such an extent that the country is not only self-sufficient in this vital basic chemicals but has surplus capacity. The industry has entered into the export market since 1991-92. The import statistics and export details of soda ash is given in **table 2.8 and 2.9.**

**Table 2.7.** List of soda ash units

| S. No | Name of unit | Location | Installed capacity (tonne) |
|---|---|---|---|
| 1 | Tata Chemicals Ltd | Mithapur, Gujarat | 7,00,000 |
| 2 | Gujarat Heavy Chemicals Ltd | Veraval, Gujarat | 4,20,000 |
| 3 | VXL India Ltd | Porbandar, Gujarat | 33,500 |
| 4 | Dharangadhra Chemical Works Ltd | Dharangadhra, Gujarat | 96,000 |
| 5 | Punjab National Fertilisers & Chemicals Ltd | Nayanangal, Punjab | 66,000 |
| 6 | Tuticorin Alkali & Chemicals Ltd | Tuticorin, Tamil Nadu | 73,000 |
| 7 | Fertilisers & Chemicals Travancore Ltd | Cochin, Kerala | 4,750 |
| | | Total installed capacity | 13,93,250 |

Source: CMIE, Market and market shares March 1995

**Table 2.8.** Import statistics of soda ash

| Year | Import ('000 tonnes) |
|---|---|
| 1980-81 | 100 |
| 1981-82 | 100 |
| 1982-83 | 65 |
| 1983-84 | 27.5 |
| 1984-85 | 15.5 |
| 1985-86 | 170 |
| 1986-87 | 14 |
| 1987-88 | 45 |
| 1988-89 | - |
| 1989-90 | - |

Source: Technology evaluation & norms study in soda ash industry, DSIR (1993)

**Table 2.9.** Export details of soda ash (in tonnes)

| Year | 1991-92 | 1992-93 | 1993-94 |
|---|---|---|---|
| Exported quantity | 50700 | 64800 | 41000 |

The compounded annual growth rate of soda ash consumption in 1970-79 and 1980-89 were 6% and 8.7% respectively. The rate of growth of demand during 1990-2000 is estimated at 8% and the estimated demand during 2000 A.D. is 2.68 million tonnes*.

## 2.3.3 *Process description*

In India, the different processes adopted for the soda ash manufacture are; (i) solvay process. (ii) modified solvay process and (iii) Akzo dry line process. Out of all soda ash manufacturing units, three units are based on Solvay process, two units follow Modified Solvay process (Dual process) and the sixth one uses Akzo dry lime process. A brief description of each of these processes are provided in this section.

### *2.3.3(i) Solvay process*

The process was invented by Earnest Solvay in 1861 and the commercial production started in late sixties. In this process, ammonia is used as the catalyst. Crude salt is dissolved in water to prepare saturated brine and then purified with lime and soda solution to remove impurities like calcium and magnesium sulphates. Purified brine is then ammoniated in the absorber. Ammoniated brine leaves absorber at 58-60°C. It is pumped to Cleaning Carbonating Tower at 32-34°C, where high pressure lean gas from lime kiln is put at the bottom. The liquor from the tower is pumped to the top of Making Carbonating Towers where high pressure rich carbon dioxide is supplied from the bottom and low pressure carbon dioxide is supplied at the middle.

Sodium carbonate (0.75 mole per mole of sodium chloride), solution of ammonium carbonate, ammonium chloride & unreacted sodium chloride, soluble sodium carbonate, carbon dioxide and traces of sulphides leave the carbonating tower in slurry form (magma). The temperature of the carbonating tower is 24-30 °C at the bottom, 55-60 °C in the middle and 25 °C at the top. Carbon dioxide gas (4-6%) leaving the carbonating tower is scrubbed with fresh brine to recover ammonia. The bicarbonate slurry is filtered under vacuum and solid is conveyed to calciner.

Sodium bicarbonate cake is heated to 190-200 °C in a rotary calciner from which rich carbon dioxide (85-90%) is recovered. The product, light soda ash (specific gravity 0.55-0.60) goes to cooler and then to storage. Part of the dry product is recycled to the calciner with crude bicarbonate to minimise caking in the dryer.

*source: *Chemical industry news, January 1994. pp 22*

Filtrate from vacuum filters is pumped to ammonia stills kept in series. In the first still, free ammonia is removed and in the second, liquor is heated with milk of lime to recover ammonia. Recovered ammonia is returned to absorber along with make-up ammonia (0.35-0.5% of final soda). The effluent from second still contains calcium chloride solution which may be sent to waste or calcium chloride recovery plant. A block diagram showing the solvay process of soda ash manufacturing is given **figure 2.4**.

*2.3.3(ii) Dual process or modified solvay process*

The principal modification of the dual process is the recovery of ammonium chloride as a by-product rather than the liberation of the contained ammonia for recycle as in the solvay process. The liquor from the bicarbonate filters is mixed with washed salt feed a to aid in precipitation of ammonium chloride which is crystallised in a refrigerator tank at 0 °C. The slurry is centrifuged and the ammonium chloride crystals are dried in a rotary drum hot air dryer and then sent for package. The modified solvay process is economical if the ammonium chloride can be used as fertiliser. The dual process is economical only when carbon dioxide gas and ammonia are available regularly at reasonable prices from nearby fertiliser units. A block diagram of Modified Solvay process is shown in **figure 2.5.**

*2.3.3(iii) Akzo dry lime process*

Dry lime process is the improvement in conventional Solvay process by adopting dry lime distillation (ammonia recovery unit). The crushed lime from the silo is fed to the prelim unit with specially designed feeders. Mother liquor, after separation of bicarbonate, is fed to prelim. In this system the heat of hydration of lime and of chemical reaction themselves are sufficient to raise the liquor to the boiling temperature. Thus the steam is used to drive out ammonia and carbon dioxide from the solution. The fine ground lime reduces the time of reaction and gives better lime utility. The steam and lime consumption is less compared to Solvay process. Dry lime distillation is used in ammonia recovery unit. The other process steps are same as conventional Solvay process. A block diagram of Akzo dry lime process is shown in **figure 2.6.**

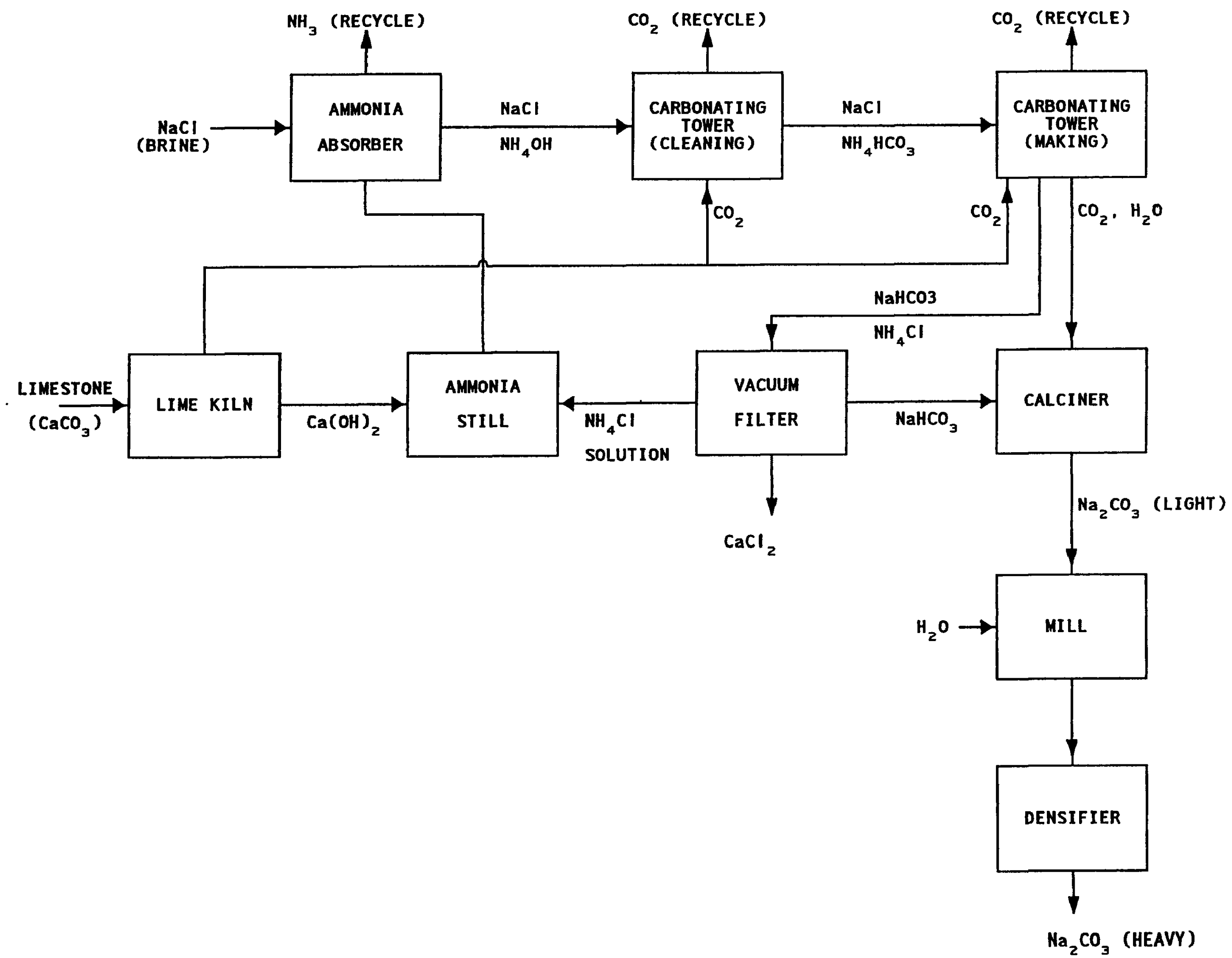



FIG 2.4 SOLVAY PROCESS

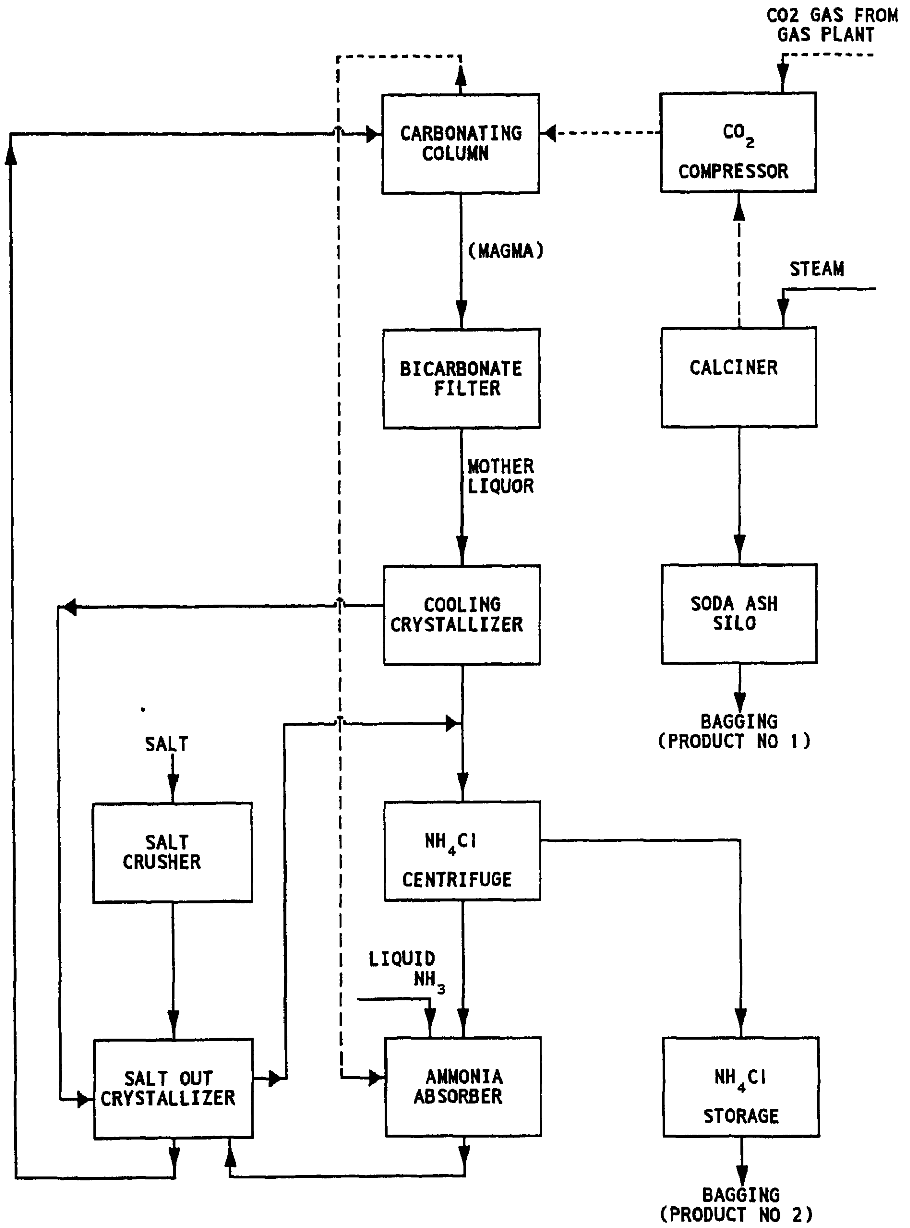



FIG 2.5 DUAL PROCESS

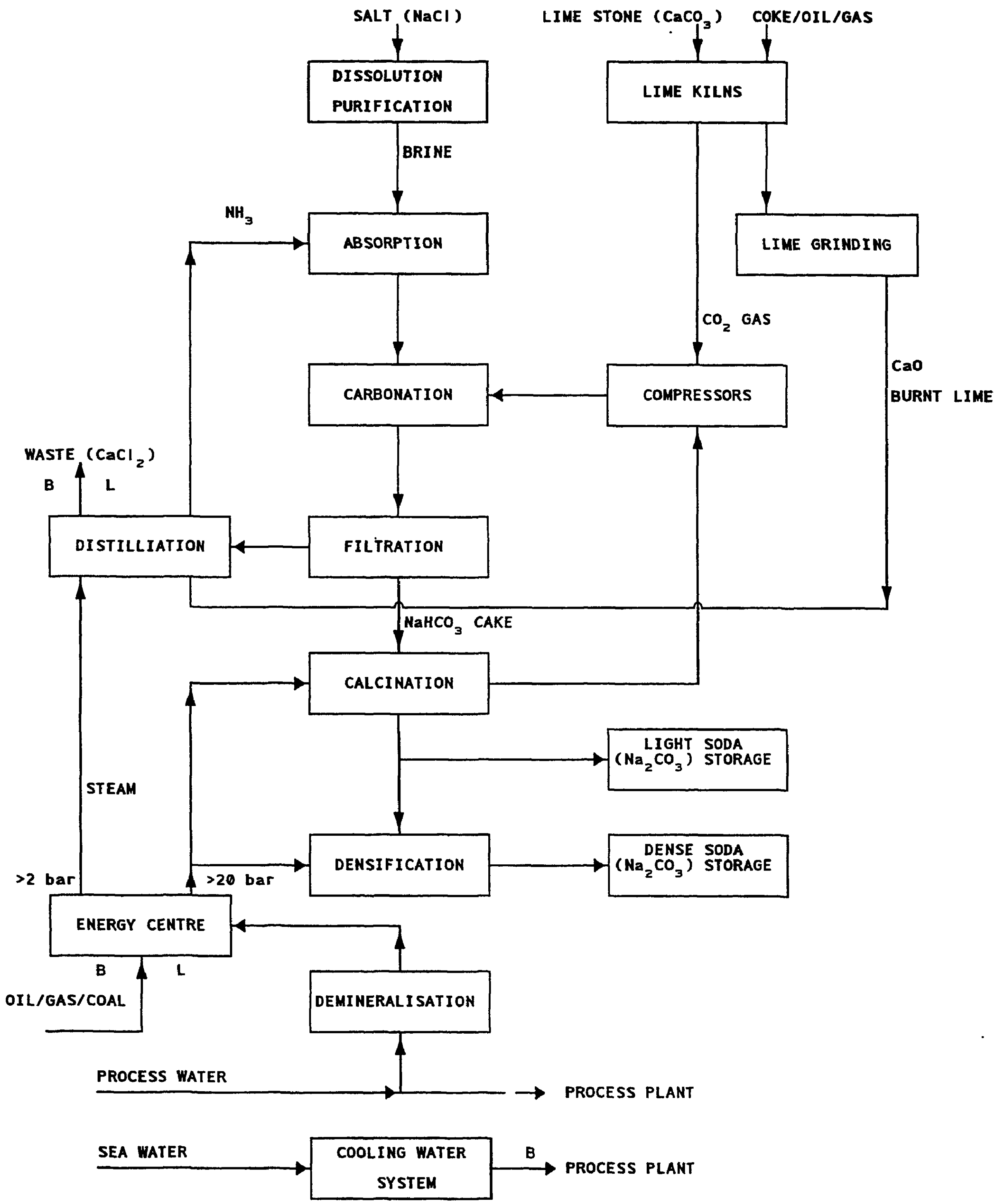



FIG 2.6 AKZO DRY LIME PROCESS

CHAPTER 3

# Energy Profile

Power cost is major cost of production. It has been increasing rapidly for last ten years. Environmental pressures will also increase costs, as may in long run increase in energy costs.

## 3.1 Caustic soda industry

Electricity is the major form of energy used in caustic soda industry. The types of energy used in different process sections of caustic soda manufacturing are given in **table 3.1.**

**Table 3.1.** Types of energy used in different process centres of caustic soda

| Area | Type of energy |
|---|---|
| Electrolysis | Electrical (DC) |
| Salt handling, brine section | Electrical |
| Chlorine compression, liquefaction & storage | Electrical |
| Caustic evaporation and fusion | Thermal and electrical |

The specific energy consumption for various process types used for caustic soda production are given in **table 3.2**. As can be seen from the table, membranae cell process consumes moderate thermal energy per tonne of output, is the most energy efficient process having minimum overall specific energy consumption.

**Table 3.2.** Process-wise specific energy consumption in 1990-91

| Process | Thermal ('000 kcal/t) | Electrical (kWh/t) | Total (kWh/t) |
|---|---|---|---|
| Membrane cell process | 675 | 2450 | 3235 |
| Mercury cell process | 318 | 3050 | 3420 |
| Diaphragm cell process | 946 | 2800 | 3900 |

Source: Technology evaluation in caustic soda industry (DSIR), 1992

The energy consumption break-up of caustic soda industry in 1990-91 is:

Electrical energy : 3015 mil. kWh

Thermal energy : 406300 mil. kcal

CHAPTER 4

# Energy conservation opportunities

The various energy conservation measures applicable for caustic soda and soda ash industry are briefly discussed below.

The viability of conversion of existing technology depends on following factors:

a. Units amenability to conversion;
b. Capacity of the plant;
c. Level of operating performance;
d. Available finance.

## 4.1 Caustic soda industry

### *4.1.1 Conversion of mercury cell process to membrane cell process*

The changing of mercury cell process to membrane cell process would reduce the specific energy consumption by 500 kWh/tonne of caustic soda. The membrane cell process is also an environmentally friendly option as it eliminates the mercury discharge in the process effluent. Considering a typical 100 tpd plant based on mercury cell technology to conversion to membrane technology, would entail an investment of about Rs 25 crores.* The estimate is based on a case study prepared in 1989-90.

### 4.1.3 Adoption of metal anode in diaphragm process

Almost all the caustic soda units have revamped the old anode assembly with metal anodes. The advantage of installing metal anodes depends on the age of the unit and the existing instrumentation system. The reduction in specific energy consumption by replacing graphite anode with metal anode along modified diaphragm are given below.

- 150-200 kWh for new plants
- 350 kWh for old plants

### 4.1.4 Advanced instrumentation

Advanced instrumentation system for better process control of the processes would also result in substantial energy saving. Although, it is difficult to accurately estimate the extent of saving, it is reported that through such measures, it is possible, to reduce the specific energy consumption of caustic soda production by around 75 kWh.

In advanced countries, the trend of changeover to membrane cell technology has been observed in plants having an average production capacity of 500 tonnes of caustic soda per day. In India, the size of most of the plants is around 100 tpd. The major barriers for adopting the membrane technology in India are (i) high cost of conversion and (ii) high foreign exchange component, as presently the membrane cell has to be imported.

### 4.1.5 Other measures

Selected details of few other energy saving measures applicable to the caustic production are outlined below for different process centres.

*i. Electrolyser section*

- Changing cell configuration from monopolar to bipolar
- Installation of catalytically activated cathode
- Change over from rubberlined to bare bottom configuration for mercury cells. As even today, many of the plants being equipped with rubberlined cells, scope exists for energy savings through their conversion to bare bottom orientation on account of reduced millivolt drops and bus losses. Cathodic Mv drop reduced to the tune of 40%.

*ii. Salt & brine section*

- Minimisation of exposed surface area of clarifiers and better lagging
- Modifications in brine pumping system
- Better handling methods for salt

*iii. Chlorine processing section*

- Better allocation of chlorine to different options such as compression & liquefaction, hydrochloric acid synthesis so as to achieve optimum operating conditions
- Improving operating conditions of liquefaction

*iv. Caustic concentration section*

- Direct pumping of hot lye to concentrators
- Use of hydrogen gas as fuel substitute in concentrator
- Improvements in caustic lye pumping system
- Waste heat recovery

*v. Electrical section*

- Installing high efficiency rectifiers
- Installation of capacitor banks to improve power factors
- Changing bus bars orientation to reduce transmission losses
- Avoidance of part load operations of motors

## 4.2 Soda ash industry

Major energy conservation measures being adopted in soda ash manufacturing industrial units are:

(i) Use of improved design of carbonating tower to increase the heating efficiency
(ii) Use of improved heat exchangers for ammonia recovery system
(iii) Use of dry lime in ammonia still for heat recovery
(iv) Use of steam tube dryer in place of oil fired calciners

## 4.3 Constraints for implementing energy saving measures

In comparison to world standards, Indian plant capacities are quite smaller. In advanced countries, 500 tpd caustic soda plants are very common. In India, most of the plants sizes are 100 tpd. This is one of the important factor hampering the priority of energy conservation activity. In the light of the interrupted severe power problem in the country, it becomes necessary to adopt technology which is most energy efficient only. While the membrane cell process is the most modern, energy efficient and pollution free, the conversion cost of existing mercury cells and diaphragm cells has become prohibitive. This is due to high cost of capital, equipment, high technology transfer fees, compounded by high import duty on capital equipment. This has impeded the progress of adopting the membrane cell technology at a faster rate in the caustic soda industry.

The consumption of raw materials and utilities is higher in Indian soda ash industry because of poor quality raw material, old plant and old technology. The main constraints that have been faced by Indian soda ash industry are:

- Lack of capital resources;
- Type of technology in operation;

  In the old units amicable matching with/of new equipment and machinery is found not suitable and sometimes not economical.

CHAPTER 5

# Environmental aspects

Most of the chlor-alkali units in the country are based on mercury-amalgam process. Caustic soda industry have made serious efforts to reduce the mercury consumption from 350 gms/tonne to 200 gms/tonne of caustic soda and taking suitable measures to bring down this level further.

## 5.1 Caustic soda industry

The nature of various pollutants generated in the caustic soda manufacture and sources are discussed in this section under the broad sub-headings.

### *Type and Source of Pollution*

#### *5.1.1 Gaseous pollutant*

The major pollutants emitted from diaphragm and mercury cell-chlorine plants include chlorine, mercury vapours and carbon monoxide. Gaseous chlorine is present in the blow gas from liquefaction, from vents in tank cars and tank containers during loading & unloading, from storage and from process transfer tanks. Other emissions include mercury vapour from mercury cathode cells and chlorine from compressor seals, header seals, and the air blowing of depleted brine in mercury cell plants. The emission standards prescribed by Central Pollution Control Board (CPCB) for the caustic soda industry is given in **table 3.7**. The level of mercury discharge along with hydrogen gas from the decomposer before and after the treatment, as prescribed by CPCB is shown in **table 5.1**.

**Table 5.1.** Emission standards for caustic soda industry

| Type of pollutant | Source | Emission limit ($mg/Nm^3$) |
|---|---|---|
| Mercury | Hydrogen gas holder stack | 0.2 |
| Chlorine | Hypo towers | 15.0 |
| Hydrochloric acid vapour & mist | Hydro chloric acid plant | 35.0 |

Source: Minimum National Standards by Central Pollution Control Board (CPCB)

**Table 5.2.** Mercury discharge with the hydrogen gas from decomposer

| Pollutant | Before treatment | After treatment |
| --- | --- | --- |
| Mercury (gm/m$^3$) | 800 | 0.01 (stipulated) |

Source: Technology evaluation in caustic soda industry (DSIR), 1992

### *5.1.2 Liquid pollutants*

The emission of mercury along with liquid effluent is the major problem with the mercury cell process. The average mercury discharge by Indian chlor-caustic units is observed to be more than 100 gm/t of caustic soda produced whereas in advanced countries the specific mercury consumption level has been brought down below 20 gm/t of caustic soda. Indian chlor-caustic units have already achieved the standard stipulated concentration of mercury in liquid effluent but it is being revised by CPCB to make it more stringent. The norm for mercury concentration in the effluent is given in **table 5.3** for different flow rate of effluent.

**Table 5.3.** Mercury in effluent

| Norm Status | Flow of effluent (m$^3$/t) | Mercury Concentration (mg/L) |
| --- | --- | --- |
| Achieved | 10 | 0.010 |
| After revision | 2 | 0.005 |

Source: Technology evaluation in caustic soda industry (DSIR), 1992

### *5.1.3 Solid pollutants*

Another source of pollutant is the emission of asbestos fines. The specific consumption of asbestos per tonne of caustic soda in diaphragm cell process is about 48 gms, which is substantially higher than world standard of about 15 gm.

### *5.1.4. Environmental control technologies*

A description of various pollution control/ effluent treatment technologies for different category of pollutants/effluents are provided below.

#### *5.1.4.1. Chlorine*

The emission of chlorine is controlled by one of the three following methods.

*(i) Recovery of chlorine from effluent gas streams.* In normal operation, every caustic soda plant generates residual gases along with chlorine. The source of the residual gases are liquefaction, storage, handling and routine servicing of chlorine equipment. These

gases must be treated to recover the chlorine. The waste chlorine is recovered by either waste absorption or by absorption in carbon tetra chloride.

*(ii) Use of gas in other plant processes.*

*(iii) Neutralisation in alkaline scrubbers*

*5.1.4.2 Mercury*

- Activated carbon treatment plant is normally used for the removal of mercury from the hydrogen stream.
- Ion exchange resin treatment process is the most efficient demercurisation process.
- In-plant control measures to minimise discharge through water route is important to reduce the use of mercury thereby reducing the cost of treatment. The total cost of waste water treatment for different capacities of caustic soda plants is provided in the **table 5.4** which includes the amortised capital cost.
- Mercury emissions from mercury cell process can be controlled by converting the process to membrane type.

**Table 5.4.** Cost of treatment for mercury removal (1991 - 92)*

| S. No | Installed capacity (tpa) | Concentration of mercury (mg/lit) | | Method of treatment | Capital cost** (Rs million) | Annuity capital cost (Rs million) |
|---|---|---|---|---|---|---|
| | | Untreated waste water | Waste water after treatment | | | |
| 1 | 16500 | 2.5 to 6 | 0.005 to 0.5 | Sodium sulphide | 375 | 56 |
| 2 | 31400 | 6 to 10 | 0.05 to 0.15 | Sodium Sulphide | 422 | 64 |
| 3 | 29000 | 7 | Traces to 0.2 (assumed as) | Amalgamation with iron filings | 375 | 60 |
| 4 | 77600 | 10 to 12 | Traces to 0.15 | Ion Exchange | 990 | 140 |

Source: CPCB Report on MINAS for mercury cell processes

*5.1.4.3 Asbestos*

- Asbestos emissions from diaphragm cell process are controlled by passing the exhaust gases through bag filter.

## 5.2 Soda ash industry

Soda ash industry generates a large quantity of solid, liquid and gaseous effluent. The effluent generated are however, non-toxic in nature. It is simple inorganic in nature and does not have any organic matter such as COD/BOD. In Solvay process, sources of

*Price of caustic soda taken as Rs 11,000 per tonne with 15% interest rate over 20 years*

effluent are mainly from ammonia still section and brine purification section. With marginal differences, the quality of effluent being discharged from all the conventional Solvay process are same and all the liquid effluent are discharged into the sea.

In Dual process, the major aqueous effluent is only from brine purification. In this process, lime kiln section ammonia still are totally dispensed with. Small quantities of waste ammonia liquor also comes out as effluent which is usually treated with lime. The norms prescribed by CPCB in MINAS are given in **table 5.5**.

**Table 5.5.** Minimal National Standards in soda ash industry

| Parameter | Quantitative limit |
|---|---|
| Total suspended solids | 6000 mg/lit |
| pH | upto 9.5 |
| Nitrogen as ammonia | 15 mg/lit |
| Temperature | 45 °C |

Source: Minimum National Standards (CPCB)

Gaseous emissions from soda ash industry are mainly carbon dioxide. Dust emanates from solid handling section of solvay process but no separate standard has been laid down. As per the norms set by CPCB, the tolerance limits for dust particulate matter in atmospheric emission is 250 mg/Nm$^3$.

CHAPTER 6

# Conclusion

In the present study, a detailed assessment was carried out with regard to caustic soda and soda ash industry in India. These chemicals find widespread applications in industries like detergents, fibres & plastics, glass, petrochemicals, pulp & paper, fertilisers, explosives, solvents, textiles and other chemicals. The energy saving potential in the chlor alkali industry is estimated at 15% of the total energy use by the sector. In the caustic soda industry, the major energy saving measure that can be implemented is to convert the existing mercury or diaphragm cell processes to membrane cell technology. This option, apart from improving the energy efficiency, will also reduce the mercury emission from existing caustic soda plants which is a cause of major concern. The average mercury discharge alongwith liquid effluent in the Indian chlor-caustic units are more than 100 gms/t as against 20 gms/t in advanced countries. In the sod ash sector, the major energy saving measures are; (i) use of improved heat exchangers for ammonia recovery system, and (ii) use of dry lime in ammonia still for heat recovery.

Based on an assessment of the sector and its comparative evaluation with the other sectors studied under the phase-I study, chlor-alkali sector is not considered to be an ideal candidate for phase-II of the project. However, some details about a select list of plants under the sector are provided in **annexure 6.01**.

# Plant data

## Caustic soda plants

### *1. DCW Ltd*

Year of commissioning : 1959

Installed capacity : 60.000 tpa

Type of process : Mercury cell process

Other products : Liquid chlorine, Trichloro ethylene and Upgraded ilmenite

| Data | Unit | 1991-92 | 1992-93 |
|---|---|---|---|
| Production | tonne | 42,331.0 | 44,285.0 |
| Capacity utilisation | % | 70.6 | 73.8 |
| Electricity consumption | mil. kWh | 169.8 | 168.9 |

### *2. Sree Rayalaseema Alkalies & Allied Chemicals Ltd*

Year of commissioning : December 1987

Installed capacity : 33.000 tpa

Type of process : Bipolar membrane cell process

Other products : Liquid chlorine and hydrochloric acid

| Data | Unit | 1991-92 | 1992-93 |
|---|---|---|---|
| Production | tonne | 30,060.0 | 27,603.0 |
| Capacity utilisation | % | 91.1 | 83.6 |
| Electricity consumption | mil. kWh | 91.22 | 86.3 |

Sector:

Product:

| | |
|---|---|
| 1 | Total no. of units |
| 2 | Total installed capacity |
| 3 | Total production (latest figure) |
| 4 | Growth rate (last 5 years) |
| 5 | Expected growth rate |
| 6 | Total energy consumption (latest year) |
| 7 | Consumption of different energy forms |
| | - Coal |
| | - Oil |
| | - Natural Gas |
| 8 | SEC |
| 9 | Financial health |
| 10 | Conservation potential |
| 11 | Structure (%) Private/PSU/Coop. |
| 12 | Vintage category |
| | <5 |
| | 5-10 |
| | 10-15 |
| | 15-20 |
| | >20 |
| + | List of energy saving options |

*Annexure 6.01*

# List of selected units for energy and environment audit

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1. Ballarpur Industries Ltd
   Shree Gopal Division
   Yamuna Nagar
   Haryana

2. Chemfab Alkalies Ltd
   Gnanananda Place
   Kolapet
   Pondicherry - 605 104

3. Grasim Industries Ltd
   P.O. Birlagram
   Nagda, M.P.

4. Punjab Alkalies & Chemicals Ltd
   SCO 125-127, Sector 17-B
   Chandiagarh - 160 017

5. Southern Petrochemical Industries Ltd
   Mandi Industrial Complex
   Manali
   Madras - 600 068

6. Standard Alkali (Chemical Division)
   Standard Industries Ltd
   Mafatlal Centre
   Nariman Point
   Bombay - 400 021

7. Tata Chemicals Ltd
   Mithapur
   Gujarat

8. Sree Rayalseems Alkalies and Allied Chemicals Ltd
Vasant Nagar
Gondiparla Village
Distt. Kurnool - 518 004 (A.P)

9. Gujarat Heavy Chemicals Ltd
Sutrapada (Near Veraval)
Gujarat

10. Turicorin Alkali & Chemucals Ltd
Tuticorin
Tamil Nadu

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